(4)

QUARTERLY REPORT
for
DARPA/ONR
HIGH TEMPERATURE SUPERCONDUCTIVITY
FIRST QUARTER FY1989

I. PROGRAM INFORMATION

Contract Number: N00014-88-C-0760

Principle Investigator: Dr. James N. Eckstein

Institution/Address: Varian Research Center
M.S. K-214
611 Hansen Way
Palo Alto, CA 94303
(415)424-5081

Report Prepared By: Dr. James N. Eckstein

Report Date: Jan. 9, 1989

II. PROGRAM SUMMARY

The overall goals of this program are to develop the technology of MBE growth of HTSC material, to optimize the performance of HTSC films with high transition temperatures and critical current densities, and to explore the development of electronic devices based on such material.

III. PROGRAM STATUS

We received our contract from ONR in the middle of November 1988 and commenced work on the contract statement of work at that time. During the first six months of the effort, we will be investigating the growth of the newer layered compounds containing Bi or Tl. This was clarified and approved in several phone calls and documented in a subsequent letter sent to DARPA and ONR. The original milestones called for the first quarter to consist of initial investigation of HTSC film growth. We had also specified looking into advanced post-growth anneal studies, although with our more recent success in developing in-situ growth, the utility of post-growth anneals will need to be evaluated. The next quarter will be devoted to continued development of the MBE *process* using the recently-completed MBE system. This is further discussed in Sec. V -- Problem Areas and VI -- Corrective Actions. In particular, we will attempt to obtain actively structured HTSC films this quarter and study the use of actively structured epitaxy to grow in-situ films of various Bi or Tl layerings.

IV. ACCOMPLISHMENTS

During the latter part of first quarter of FY 89, we continued (now under DARPA/ONR contract support) to study both fundamental and practical issues involved in the heteroepitaxial in-situ growth of copper-containing layered perovskite compounds. This included continued analysis of previously grown films. A significant insight into the MBE growth process was obtained by detailed study of lattice image transmission electron microscopy of one of our earlier as-grown superconducting films of Dy-Ba-Cu-O. In particular, the interplay between kinetic control and the tendency toward thermodynamic equilibrium was evident. This has lead to important insights in understanding the process by which layered, superlattice-like structures in these systems can be grown.

To review briefly, it is the aim of our approach to use kinetic control available in MBE from beam shutters and stable sources to atomically layer the superlattice-like structure of

extended unit cell HTSC compounds. To do this, active sources of oxygen are employed to ensure the completion of at least the necessary degree of oxidation and the beams of the constituents are turned on and off using mechanical shutters to layer the constituent species and to provide kinetic control of the growth process.

The attached figure is a copy of a lattice image TEM of one of our in-situ superconducting films, VSC-125. The TEM work was done by S. K. Streiffer and J. C. Bravman of the Materials Science Department at Stanford. The image shows the first several hundred angstroms of epitaxial growth on top of the $SrTiO_3$ substitute and provides important and heretofore unknown information about the processes at play during epitaxial growth of these kinds of compounds, employing kinetic control. We believe the conclusions drawn here will be relevant in the case of similar compounds, such as those in the Bi/Tl families of currently being studied.

The figure shows some regions that were damaged and hence provided no lattice image. These are principally in the upper left-hand corner and upper right-hand corner. The lower part of the figure is an image of the $SrTiO_3$ substrate. The film begins with the dark bands that, especially in the middle, are separated by lighter bands of approximately half the thickness of the darker bands. Further up, approximately 100 Å above the interface, a tripled unit cell that extends many lattice constants in transverse dimension is visible. In fact, this can be found in about half of the upper part of the image. At about the same level where the tripled unit cell is strongly evident, another region, epitaxially arranged with respect to the tripled unit cell region, can be observed with a doubled unit cell structure. In addition, there are occasional indications of a 2-4-8 type layering as well. With all these phases, however, no discernable "grain boundary" can be seen. Instead, at each level the different "phases" locally present appear to be atomically in registry with the rest of the film. This is also consistent with the RHEED patterns observed during growth that showed sharp streaks indicative of the growth of a smooth epitaxial film.

The relative locations of the various patterns and features gives important information as to the physical processes occurring. To begin with, the light and dark bands observed near the interface can be identified as layers that contain Dy and Ba atoms, respectively. These features are somewhat diffuse and their thicknesses indicate the flux bursts were chosen incorrectly. Apparently there were too many Dy and Ba atoms/cm^2 incident during each burst, and the resulting kinetically controlled structure that was frozen in the first 100 Å of film evidences this by the larger than desired average spacing between, e.g., the light bands. Even

though the growth temperature, ≈580°C, is probably too low to promote vertical diffusion, surface diffusion undoubtedly exists. The occurrence of sharp 1-2-3 structure at about the same time as the occurrence of a sharp doubled unit cell indicates that a type of phase separation is occurring on the growing surface that even so results in the growth of single crystal-like layers. Statistically, different regions must form, after some period of time, that propagate in the growth direction to accommodate the nonideal shuttered flux bursts into regions of stable equilibrium phase material. Thus at these temperatures, getting "close" to the correct incident flux seems to be enough to allow thermodynamic forces to drive the segregation of phases via mobile surface species. Presumably, the degree of stability of a particular phase, or equivalently the extent to which the free energy of a particular arrangement is minimized relative to other configurations, determines the strength of the thermodynamic restoring forces seeking to promote those configurations via surface diffusion. This, coupled with the stoichiometry of the shuttered fluxes, ultimately determines the crystallographic structure grown.

This result is particularly interesting since there has always been some concern about what will occur if the shuttered flux bursts, especially of the larger atoms such as Dy, Ba, Bi, Sr, Ca, etc., are not accurately adjusted to deposit exact integral or multiple monolayers of the desired constituents. More precisely, the question may be rephrased as just how close to the absolutely correct flux is close enough and what physical processes occur to give some process latitude. In the case of the film pictured here, the flux bursts inferred from banding near the substrate were off by as much as 50%. During the first few layers, the metastable structure that resulted was frozen in. This structure is clearly metastable and is dominated by kinetic effects; however, it is also heteroepitaxial and single crystal-like. This picture shows that surface-mediated epitaxial phase separation in a single-crystal-like film is the process by which "extra atoms" are accommodated. It would suggest a greater tendency than had been expected for some type of phase separation to occur, in this case by a surface mediated process, maintaining an epitaxial film. Once the phases nucleated, the driving force of the shuttering presumably maintained the crystallographic orientation of the tripled unit cell material in an approximate layer by layer manner.

V. PROBLEM AREAS

On the practical growth technology front ,we focused our efforts in developing a process for the in-situ growth of higher transition temperature bismuth/thallium-containing compounds. Here we discovered even more difficulty in controlling the stoichiometry of the

grown film and absolute beam fluxes of the constituent sources than we had experienced with our work in growing the 1-2-3 compound.

After a careful series of test runs and a re-examination of all our previous in-situ growths (1-2-3 phase material; Bi-containing 2212 and 2223-like material), we discovered the cause of as well as a solution for those difficulties. While we examined several alternatives, the recent increased difficulty in flux control, and hence of course, composition and kinetically define layering control, was attributed to gas phase collision in the growth chamber scattering the source beams caused by a too-high O_2 background pressure. The large background oxygen pressure was due to the mass flow required for operation of our plasma source coupled with the rather poor pumping speed of the growth chamber. The reason why the bismuth family materials are more sensitive to this effect was also discovered.

During the early stages of this program when metal films were deposited at vacuums of $5 \cdot 10^{-6}$ Torr or better and subsequently annealed to form HTSC layers, it was observed that very good and reproducible compositional control was obtained by first measuring the beam pressure of each source individually and then relating beam pressure to beam flux using constants of proportionality for each source determined experimentally from microprobe measurements. These constants, once determined, were not observed to change, and films grown in this way had the desired composition to a high degree of precision. During the following experiments in which our plasma generator was used, the O_2 mass flow required for the plasma source to remain lit coupled with the pumping speed of the system led to a higher chamber pressure, between 1.5 to $4.0 \cdot 10^{-4}$ Torr. In-situ growth of copper-containing perovskite films was obtained, and some of these films (such as the one described earlier in this report) were superconducting. In order to obtain stoichiometric films, however, roughly three times as much of a copper flux was required than would have been predicted based on calibrations of the low pressure runs. Since only the copper flux had to be corrected (for at that time an unknown reason), it was relatively easy to obtain reproducible film stoichiometries. When growth of bismuth-containing material was started, much the same thing happened. It was relatively easy to obtain reproducible co-deposition of the metal constituents when the deposition occurred at low pressure. During our attempts at growing in-situ films of Bi-Sr-Ca-Cu material (i.e., 2212 and 2223), very significant control problems emerged that we finally concluded couldn't be adequately corrected in the existing system. Some layered films with approximately the correct stoichiometry and X-ray structure were obtained, but these were semiconducting, and the run-to-run reproducibility was poor.

Three possible causes for these problems emerged. First, it might have been the case that the sticking coefficient for each action at ≈580°C was highly dependent on the degree of surface oxidation, and therefore the details of the operation of the plasma source. The internal electrodes of the source were know to age, giving somewhat of a time-dependent flux of reactive oxygen. Second, it might have been the case that the high oxygen pressure caused some encapsulation by a nonvolatile oxide, particularly of the molten Cu, that reduced the source flux and therefore required correction. Finally, it was proposed that gas phase collisions gave rise to the problem.

The first possibility is somewhat difficult to rule out completely. Our measurements over several tens of runs, however, indicate no significant effect that can be unambiguously related to the substrate temperature either in the growth of 1-2-3 phase or bismuth-containing material.

The second possibility is known to be a potential problem. Such effects on the copper flux have been documented. However, they are not of such a magnitude as to explain the phenomena. Furthermore, in the case of the bismuth-containing material, large corrections were required for Ca and Sr in addition to Cu in order to obtain stoichiometric films grown at background pressures of $2 \cdot 10^{-4}$ Torr, but neither the Ca nor Sr sources showed any "encapsulation" effect. In order to rule out this completely ,a differentially-pumped source of Cu was used. This did not appreciably alter the large corrections required.

The gas phase collision hypothesis was tested by depositing two films, sequentially, one at low pressure and one at high pressure. A ratio of cations designed to give the 2212 composition was chosen, and careful beam pressure measurements were made before and after each run. One run was deposited with the background pressure less than 10^{-6} Torr, while the other was done with the background controlled to $2.0 \cdot 10^{-4}$ Torr. The composition of the films was significantly different. A subsequent set of runs indicated that if gas phase collision was stopping Ca, Cu and Sr from reaching the surface, it had little effect on Bi_2O_3. This is understandable since Bi_2O_3 is quite massive (MW = 466) and would be only slightly affected by collisions with the much lighter O_2 molecules (MW = 32). Apparently the lighter atoms Cu (MW = 63.5), Sr (MW = 87.6) and Ca (MW = 40.1) were more affected by the oxygen background pressure. Collisions that would knock a lighter atom out of the required forward cone trajectory would not do so for the heavier species. Additionally, the atomic radius of these lighter atoms ranges from 1.57Å for Cu to 2.23Å for Ca to 2.45Å for Sr, leading to significantly different collision cross sections with O_2 molecules.

At $2 \cdot 10^{-4}$ Torr, only one in 15 Ca atoms, one in three Cu atoms and one in ten Sr atoms made it from their respective sources to the substrate. In practice, to simultaneously make such large corrections, factors of three to 15 in beam fluxes based upon measurements such as microprobe and beam pressure readings that themselves have inherent error bars could not be expected to work reproducibly to the required precision.

In order to further clarify the situation, an additional run was done at an intermediate pressure of $5 \cdot 10^{-5}$ Torr. Since the probability of suffering a gas phase collision in a given distance depends exponentially on the pressure, the transmission coefficients, t_i, would be expected to change to $t_i^{1/4}$ relative to what was measured out at $2 \cdot 10^{-4}$ Torr. Within experimental error bars, the results of the film's microprobe analysis was consistent with this being the case.

VI. CORRECTIVE ACTION

The obvious solution was to accelerate the corporate-sponsored effort to complete our new growth chamber which, among other features, has ten times the gas pumping speed of the old chamber. As of this writing the new chamber has been retrofit to the MBE system and is undergoing calibration tests. Due primarily to the extensive UHV experience available within this organization, we anticipate continued MBE growth *process* development to resume by mid-January aimed at growing layered bismuth compounds, in-situ, with T_cs in excess of 100K. Since we discovered and are now correcting a problem so great in magnitude that it alone could explain our difficulties in obtaining in-situ superconducting bismuth-containing films, we have elected not to pursue the use of thallium yet. This remains an option that we will consider if satisfactory results are not obtained in the near future.

VII. GOALS FOR NEXT REPORTING PERIOD

- Develop reproducible process for accurately layering Bi family of compounds
- Obtain epitaxial in-situ grown superconducting films on $SrTiO_3$

VIII. FINANCIAL STATUS

Due to the late date at which we began and the occurance of the holidays, only about $10,000 was directly charged by Varian to the contract. Possible charges on the Stanford

subcontract will be determined when that contract is finalized. We anticipate spending an additional $621,000 this fiscal year.


100 Å
Dy-Ba-Cu-O
Film